



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

California GAMA Special Study: Application of multi-tracer methods to determine age distribution in nitrate-contaminated wells

A. Visser, A. Deinhart, J. Moran, R. Bibby, S. Roberts,
M. Singleton, G. Eppich, B. Esser

March 30, 2015

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.



**GAMA: AMBIENT GROUNDWATER
MONITORING & ASSESSMENT PROGRAM
SPECIAL STUDY**



California GAMA Special Study:
Application of multi-tracer methods to determine age distribution in nitrate-contaminated wells

By Ate Visser, Amanda Deinhardt, Jean E. Moran*, Richard K. Bibby, Sarah Roberts, Michael J. Singleton, Gary R. Eppich, and Bradley K. Esser*

*Lawrence Livermore National Laboratory
California State University, East Bay

Prepared in cooperation with the
California State Water Resources Control Board
LLNL-TR-xxxxxx

March 2015

Suggested citation:

Ate Visser, Amanda Deinhart*, Jean E. Moran*, Richard K. Bibby, Sarah Roberts, Michael J. Singleton, Gary R. Eppich, and Bradley K. Esser (2015) **California GAMA Special Study: Application of multi-tracer methods to determine age distribution in nitrate-contaminated wells.** Lawrence Livermore National Laboratory LLNL-TR-XXXXXXX, xx pp.

California GAMA Special Study: Application of multi-tracer methods to determine age distribution in nitrate-contaminated wells (LLNL-TR-XXXXXXX)

Ate Visser, Amanda Deinhardt*, Jean E. Moran*, Richard K. Bibby, Sarah Roberts, Michael J. Singleton, Gary R. Eppich, and Bradley K. Esser

*Lawrence Livermore National Laboratory, *California State University-East Bay*

Prepared in cooperation with the State Water Resources Control Board

Contents

1. Introduction	2
1.1 Study objectives and design	2
1.2 Groundwater residence time tracers	2
1.2 Study Setting.....	4
2. Methods	5
2.1 Sample collection.....	5
2.2 Hydrogeologic Setting.....	7
3. Results and Discussion	10
3.1 Field Parameters, Stable Isotopes of Water, and Major Ions.....	10
3.2 Nitrate, Excess Nitrogen, and Isotopes of Nitrate	12
3.3 Age Tracers	15
3.4 Lumped Parameter Models and Nitrate Forecasting	19

This page intentionally left blank

California GAMA Special Study: Application of multi-tracer methods to determine age distribution in nitrate-contaminated wells (LLNL-TR-XXXXXXX)

Ate Visser, Amanda Deinhart, Jean E. Moran*, Richard K. Bibby, Sarah Roberts, Michael J. Singleton, Gary R. Eppich, and Bradley K. Esser* Lawrence Livermore National Laboratory,

**California State University-East Bay*

Prepared in cooperation with the State Water Resources Control Board

Key Points

Suggested citation:

Ate Visser, Amanda Deinhart*, Jean E. Moran*, Richard K. Bibby, Sarah Roberts, Michael J. Singleton, Gary R. Eppich, and Bradley K. Esser (2015) **California GAMA Special Study: Application of multi-tracer methods to determine age distribution in nitrate-contaminated wells.** Lawrence Livermore National Laboratory LLNL-TR-XXXXXXX, xx pp.

1. Introduction

1.1 Study objectives and design

Rising nitrate concentrations in public supply wells continue to present a serious threat to drinking water in California. Public supply wells nearly always exhibit a broad distribution of groundwater age and in many settings, the age distribution determines the evolution of nitrate concentrations in produced groundwater. Wells exhibiting very young apparent groundwater age are expected to show a rapid response to nitrate applications at the surface. Wells with intermediate ages may show a slower response and long term upward trends following nitrate application. Wells with old ages are expected to show continuous dilution of nitrate by water that is very low in nitrate - a recent GAMA special study (Visser et al., 2013) showed that California public supply wells producing 'tritium-dead' groundwater, in which more than 80% of the water was recharged before 1950, nearly always produce low-nitrate groundwater. Groundwater age distributions may therefore be applied to forecast future nitrate concentrations in public supply wells when combined with historical records of nitrate concentrations for the wells. Examination of age distributions and nitrate concentrations can also be used to predict the expected effects of a reduction in nitrate loading to the water table on concentrations at a well, following implementation of best management practices or following changes in land use.

In this study, public supply wells from Turlock, CA were sampled for multiple age tracers. Multiple tracers are applied to characterize differently-aged groundwater components in an effort to constrain the age distribution to the extent possible. Additional analyses conducted were related to the source and fate of nitrate, since nitrate applied at the surface may not be transported conservatively if denitrification is taking place. The land use history in and near Turlock was examined in order to qualitatively assess the history of potential sources of nitrate to groundwater. Finally, tracer observations and records of nitrate concentrations in wells were input into Tracer LPM (Jurgens et al., 2011), a spreadsheet program that allows testing of various lumped parameter models of age distributions, visualization of age distributions and calculated apparent ages, and forecasting of future nitrate concentrations in individual wells.

1.2 Groundwater residence time tracers

Dissolved noble gases (helium, neon, argon, krypton and xenon) in groundwater provide a snapshot of groundwater recharge conditions. Noble gases are transported conservatively in saturated media, providing a long term record. Altitude and temperature control noble gas solubility. Water level fluctuations cause bubble entrainment in the unsaturated zone and noble gas super-saturation, known as excess air. These properties make dissolved noble gases especially well-suited to examining recharge processes and groundwater transport [Manning and Caine, 2007; Plummer et al., 2001; Manning and Solomon, 2005; Rademacher et al., 2001, 2005; Singleton and Moran, 2010].

The primary sources of noble gases dissolved in natural waters are equilibration of water with the atmosphere and the decay of several radioactive isotopes (OZIMA and PODOSEK, 2002; PORCELLI et al., 2002). The abundances of the heavier noble gases (Ne, Ar, Kr, Xe) in groundwater are due primarily to atmospheric equilibration of water during groundwater recharge and excess air formation, and their elemental abundances are directly related to the temperature and altitude of the groundwater recharge location.

Helium isotopes (^3He and ^4He) in groundwater are derived from several different sources: equilibration with the atmosphere (^3He and ^4He), excess air from bubble entrainment in the unsaturated zone (^3He and ^4He), nuclear fission of ^6Li (nucleogenic ^3He) associated with the production of ^4He by U-Th decay (radiogenic ^4He)(Schlosser et al., 1989), mantle helium (^3He and ^4He) and tritium decay (tritogenic ^3He). The abundances of the helium isotopes are directly related to the age of the sample – the time since last contact with the atmosphere.

When combined with measurements of tritium, helium isotopes provide a means of quantifying the apparent $^3\text{H}/^3\text{He}$ groundwater subsurface residence time, or groundwater age, over a time scale of about 55 years. Radiogenic helium is also a tracer for groundwater age, typically in the range of 10^3 to 10^6 years (Marine, 1979).

Complications associated with terrigenic sources of helium in California groundwater basins call for alternate age tracers of young groundwater. The production and processing of nuclear fuel releases ^{85}Kr into the atmosphere, and atmospheric concentrations of ^{85}Kr have increased steadily since the advent of the nuclear age (Figure 1). Groundwater studies have demonstrated that ^{85}Kr is a reliable age tracer and a valuable complement to tritium (Ekwurzel et al., 1994). ^{85}Kr has a half-life similar to that of tritium but has dramatically increased in the atmosphere over the last fifty years, while tritium concentrations in precipitation peaked in the 1960s. Collecting and preparing samples and analyzing ^{85}K , however, is complicated because of its low isotopic abundance (10^{-15} of total krypton) and the low concentration of total krypton in water. The process involves extracting and collecting dissolved gas from several cubic meters of groundwater at the point of collection, followed by the separation of Kr from hundreds of liters of collected gas. Analysis involves counting ^{85}Kr on special low-level scintillation counters.

Sulfur-35 has a relatively short half-life of 87 days, and its presence in groundwater suggests that the water is likely from recent precipitation. ^{35}S forms in the atmosphere through cosmic ray spallation with ^{40}Ar . In the atmosphere it is oxidized to sulfate ($^{35}\text{SO}_4^{2-}$), and through precipitation, falls onto the land, and infiltrates into the groundwater. Sulfate, in this anionic form, is relatively conservative in the groundwater and may be a useful tracer for shallow groundwater systems.

Carbon-14 is a useful tracer for dating post-modern, very old groundwater. The half-life of ^{14}C is 5,730 years, and the age determination limitation is approximately 40,000 years. ^{14}C is produced in the atmosphere (almost constantly) due to interaction of cosmic rays with atmospheric nitrogen. The radioactive carbon bonds with oxygen to form CO_2 , which then infiltrates into the aquifer via precipitation. The geochemistry of ^{14}C in the groundwater is complex and ages are apparent. The apparent age determination is calculated by using the following equation: $t = -8267 \log (\delta^{14}\text{C}_{\text{final}} / \delta^{14}\text{C}_{\text{initial}})$.

Table 1. Environmental tracers of groundwater age applied at City of Turlock wells

Isotope	Half-life	Approximate Application Range
Sulfur-35	87.2 days	1.5 years
Krypton-85	10.8 years	60 years
Tritium/Helium-3	12.32 years	60 years
Radiogenic Helium-4	--	100,000 years
Carbon-14	5,730 years	40,000 years

1.2 Study Setting

Turlock, California (population 68,000) is located in Stanislaus County, one of California's top ten agriculture counties and one of the top producers of agricultural commodities in the nation. Agriculture is the County's most profitable industry, and applied fertilizers are factor likely contributing to high levels of nitrate contamination in the groundwater. Turlock's top crops (per acre) are hay and almonds (City of Turlock, 2012), which are large users of N fertilizers. In 2012, Turlock used over 46,000 acre-feet of groundwater for urban purposes and 460,000 acre-feet of groundwater for agriculture. Groundwater accounts for all of Turlock's drinking water, and with average nitrate levels rising from 12 mg/L to 21 mg/L in the last twenty years, contamination has become a major concern with regard to the drinking water supply. Within the last ten years, two wells were closed due to nitrate levels exceeding the MCL of 45 mg/L (TGBA, 2008). Figure – shows one example of the rising trend of nitrate from a production well in Turlock (GAMA Geotracker, 2014).

Nitrate As NO3 Results for 5010019-035

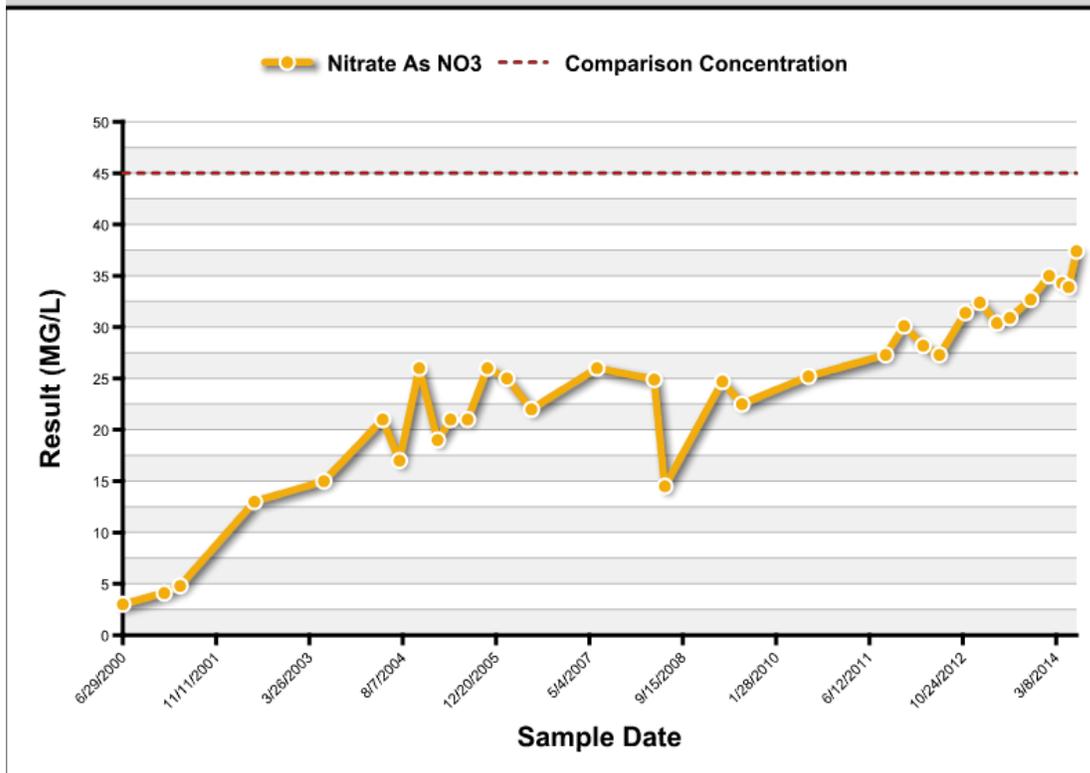


Figure 1 GeoTracker graph showing the nitrate trend from sampled well 35, Turlock

2. Methods

2.1 Sample collection

Water samples were collected according to LLNL-GAMA standards (Moran et al., 2004), directly from the sampling port of the production wells. At each well, field parameters were measured (upon stabilization) during collection using an YSI multi-probe field meter, these parameters include: pH, temperature (C°), conductivity ($\mu\text{S}/\text{cm}$), oxygen-reduction potential (mV), and dissolved oxygen (mg/L).

A groundwater sample for analysis of dissolved noble gases is collected by pumping water through a soft copper tube (0.95 cm diameter, 35 cm length) that is subsequently sealed under back-pressure with steel pinch clamps to create a gas-tight cold weld. The cold-welded copper tube typically contains 9.75 grams of water, determined accurately by weighing tube and clamps before and after analysis.

A tritium analysis requires a 1 liter groundwater sample suitable for analysis of tritium is collected without filtration in a one-liter glass bottle. The sample is stored without refrigeration or preservation (acidification, etc.).

Water samples for stable isotopes were collected using 30 mL, clear, square glass bottles with Qorpak™ polyseal-lined cap. The glass bottles were rinsed three times with water directly from the sampling port before being filled. These samples were stored at room temperature as CSU East Bay.

For analysis of sulfur-35, one 20 L carboy was used to collect the water. Tygon tubing was directly attached to the sampling port and the other end of the tube was hose clamped to a .45 micron high capacity plastic disposable filter. The carboy was filled a third of the way up, shaken, and emptied. This procedure was done three times before the final 20 L water sample was collected. These samples were stored at room temperature at LLNL.

For analysis of carbon-14, water was collected in 250 mL amber glass bottles with blue septum caps. These samples were filtered with a high capacity plastic disposable filter using the same filtering procedure as sulfur-35. The amber bottles were rinsed out three times before the final sample was taken with zero headspace. These samples were stored on ice in the field and were refrigerated upon arriving at the LLNL.

Water samples for major anions and isotopes of nitrate were collected in two separate triple rinsed 125 mL Nalgene plastic bottles. Both samples were filtered using a high capacity plastic disposable filter. These samples were stored on ice in the field and samples for major anions were refrigerated and samples for isotopes of nitrates were frozen at LLNL.

For major dissolved gases water was collected in 3, 40 mL amber VOA vials (VWR TraceClean™, amber borosilicate; 0.125-in septa liner), with zero headspace. The samples were filled directly from the sampling port with no direct contact to the port. Samples were immediately put on ice in the field and were refrigerated upon arrival at LLNL.

Water samples for boron analysis was collected using 50 mL plastic centrifuge tubes. The centrifuge tubes were rinsed three times directly from the sampling port before obtaining the final sample. These samples were stored at LLNL at room temperature.

Water samples for carbon-13 was collected in 40 mL amber VOA vials (VWR TraceClean™, amber borosilicate; 0.125-in septa liner), with zero headspace. These samples will be filtered using the same filtration method as sulfur-35. They will be put on ice in the field and will be refrigerated upon arrival at the lab.

Water samples for major and trace cations will be collected in 125 mL plastic Nalgene bottles. The water samples will be filtered using the same filtration method for sulfur-35. The bottles will be rinsed three times before collection of the final sample. Samples will be put on ice in the field, are to be acidified with ultra-pure nitrate acid to a pH of 2 and refrigerated upon arriving at the lab.

Large volume (2000-4000 L) samples were collected for ⁸⁵Krypton analysis using a membrane contactor gas extraction system (GES) as described in Visser et al., 2015.

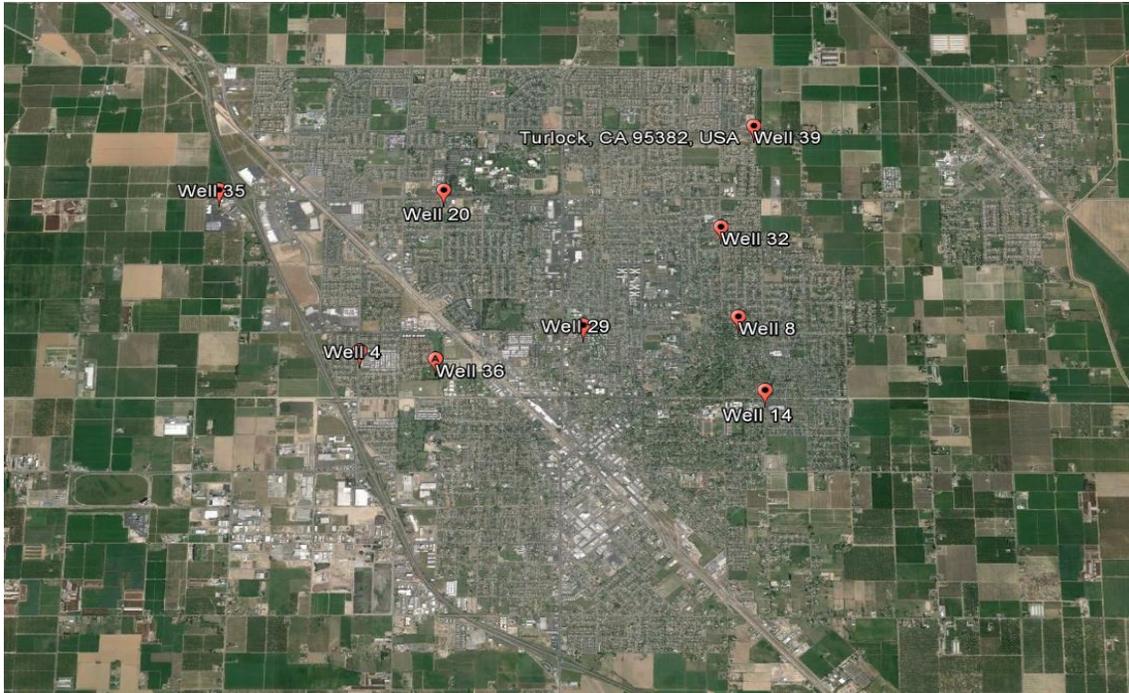


Figure 2: Map showing production wells in Turlock, CA which were sampled for age and nitrate tracers.

2.2 Hydrogeologic Setting

The Turlock groundwater basin is characterized as a subbasin of the San Joaquin Valley Groundwater Basin. Unconsolidated and consolidated sedimentary deposits are the main hydrogeologic units that make up the Turlock Subbasin (TGBA, 2008).

The Lone Formation, the Valley Springs Formation, and the Mehrten Formation make up the consolidated deposits. They are listed in decreasing age with the Lone Formation being the oldest (Eocene Epoch) and the Mehrten Formation being the youngest (Miocene to Pliocene Epochs). The Mehrten Formation is predominately composed of andesitic tuff and gravel. Rhyolitic ash and clay are the main lithologies of the Valley Springs Formation. The Lone Formation is primarily made up of sandstone clay (Arkley, 2009). These formations are located in the eastern region of the Subbasin and produce little water to wells, however, the Mehrten Formation is a significant aquifer that typically yields large amounts of water to wells (TGBA, 2008).

The unconsolidated deposits that cover the Mehrten Formation are the Turlock Lake Formation, the Riverbank Formation and the Modesto Formation. These deposits are listed in decreasing age with the Turlock being the oldest (late Pliocene to early Pleistocene), and the Modesto Formation the youngest (late Pleistocene). The main lithologies of these formations are granitic sands above stratified silt, and sands (Arkley, 2009). Both the Turlock and Modesto Formations contain lake and floodplain deposits that act as aquitards. The Corcoran Clay is a major aquitard within the Turlock Formation. This aquitard is the uppermost portion of the Turlock Formation and is in contact with the Riverbank Formation, however, it is only found in the western section of the Turlock Subbasin. The Corcoran Clay separates the upper unconfined aquifer and the lower confined aquifer.

The upper unconfined aquifer is the water table aquifer and is approximately 150 feet thick. This aquifer supplies the western part of the Subbasin with water for agriculture and private domestic

wells. The unconfined aquifer provides water for wells that have depths less than 200 feet. The confined aquifer is found in deeper hydrogeologic units and is under pressure by the Corcoran Clay. The aquifer is semi-confined on the eastern side of the Subbasin. This aquifer provides a large amount of water for agriculture and municipal purposes. Wells that are deeper than 200 feet are generally supplied by this aquifer (TGBA, 2008). A cross-section of the Turlock Subbasin is shown in Figure 3.

Groundwater levels in Turlock have decreased substantially over the last 40 years. The water table has dropped over 100 feet since the 1970's due to a change of rangeland to permanent crops as well as residential and industrial demands (Sbranti, 2013). Between 1997 and 2006, groundwater storage decreased by an estimated 21,500 acre-feet/year (TGBA, 2008). Irrigation from the Tuolumne River is the largest contributor of inflow to the groundwater basin and is essential for sustaining groundwater storage.

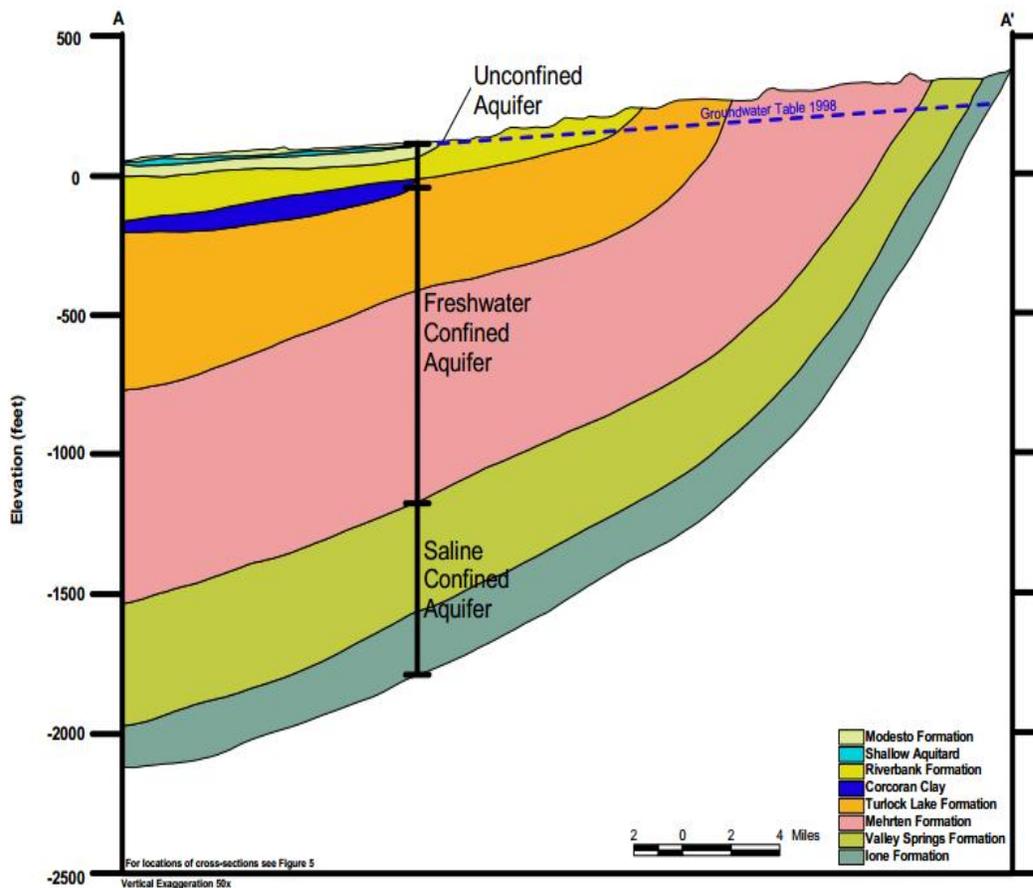


Figure 3: Schematic East-West cross section of the Turlock Subbasin (TGBA, 2008).

Climate

Turlock has a Mediterranean type climate, which is characterized by dry, hot summers and wet, cool winters. Precipitation mainly occurs between November and March. In this part of the

region, rainfall varies each year, with the average annual precipitation approximated to be 11-13 inches. Since most of the precipitation occurs in the winter, a majority of crops and orchards are dependent on irrigation during the remaining seasons. Although rain fall does not completely fulfill water demands, it does add to groundwater recharge. Thus, the groundwater system will have some component of water that originated from precipitation.

Land Use and History

Turlock’s history is rooted in agriculture. Farming began in the mid 1800’s, and agricultural activities intensified in 1887 with the creation of the Turlock Irrigation District. Turlock was incorporated as a town in 1908, with the original downtown centered around the railroad station. Trains and refrigerated shipping enabled farmers to advance the regions agricultural practices. The first crop census conducted in 1904 showed that 98% of Turlock’s irrigated farmland was alfalfa (Fradkin, 1997).

As Turlock urbanized, the city expanded outward, and farmland became residential and commercial areas. Figure 4 shows the growth pattern of Turlock from 1907 to 2008. Currently, there are 8,900 acres within city limits and an additional 5,800 acres of land outside the city limits that are contained within Turlock’s Planning Area. Land use is dominated by agriculture in the Planning Area, with over 6,260 acres (43%) of total land use (City of Turlock, 2012). Regional crops include almonds, grain/hay, truck and berry crops, and other nuts and fruits, with almonds covering over 155,000 acres in Stanislaus County – by far the largest in size and revenue (SCACR, 2012).



Figure 4. Land use pattern in the Turlock area from 1907-2008, with residential/commercial areas shown in black.

Public Water Supply Wells

The City of Turlock is entirely dependent upon groundwater for its municipal and industrial supply with 16(?) active wells fulfilling the demand. The criterion for choosing study wells was based on getting spatially distributed wells, including a distribution that covers the depth range that is tapped by the public supply wells. Well screen information is shown schematically on figure 5. Public supply wells with long and variable well screen intervals typically exhibit broad age distributions that result from mixing of water, either in the wellbore or in the aquifer, or both.

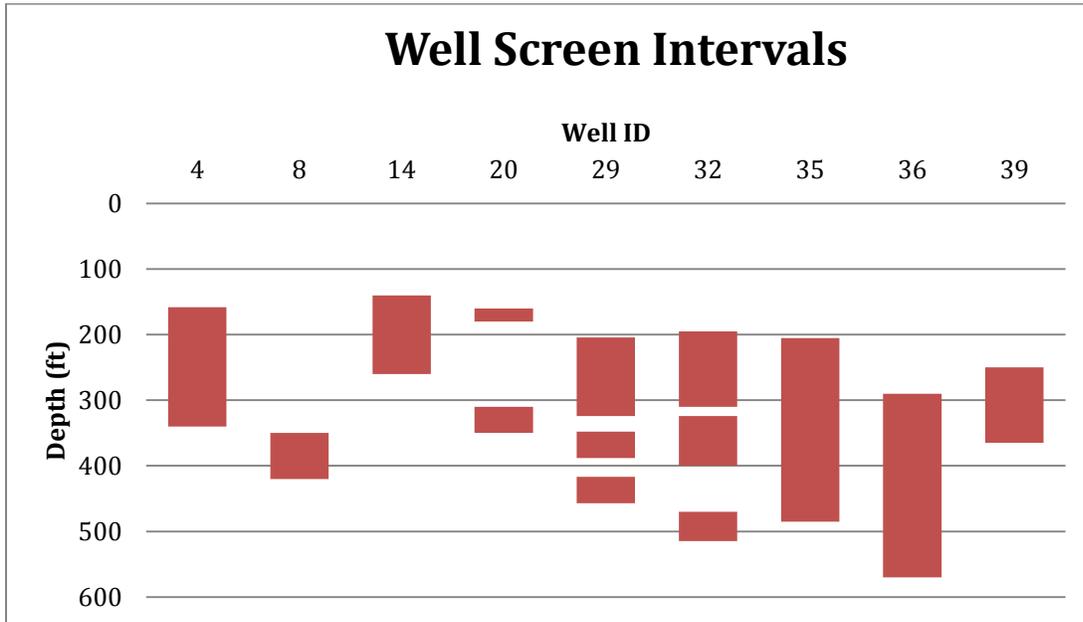


Figure 5. Schematic representation of open, perforated intervals for the public supply sampled for this study.

3. Results and Discussion

3.1 Field Parameters, Stable Isotopes of Water, and Major Ions

Results of parameters measured in the field are shown in Table 2. Of note are dissolved oxygen levels between 2.4 and 3.8 mg/L, and specific conductance levels between 0.264 and 0.378 mS/cm, except for Well 36. Well 36 stands out as having higher specific conductance, very low dissolved oxygen, and a somewhat higher discharge temperature than the other wells. (The low pH observed in Well 35 is not apparent in historical data from GeoTracker.)

Table 2. Results of field parameters at sampled wells.

Sample ID	Well	pH	Dissolved Oxygen (mg/L)	Temperature (°C)	Specific Conductivity (mS/cm)	ORP (mV)
110956	8	7.85	3.72	22.01	0.264	148.6
110957	39	7.96	3.82	21.19	0.283	169.5
110958	20	7.63	2.98	21.41	0.278	288.0
110959	29	7.89	2.65	21.78	0.271	156.0
110960	36	7.74	0.46	23.75	0.701	110.0
110961	14	7.67	3.07	21.20	0.378	139.9
110962	4	7.84	2.48	20.89	0.325	145.8
110963	35	5.55	2.40	20.67	0.341	227.9
110964	32	7.81	3.08	21.30	0.364	95.7

Stable isotopes of the water molecule group tightly around mean values of -11.7‰ for $\delta^{18}\text{O}$ and -81.4‰ for δD , close to the global meteoric water line and significantly lighter than the values expected for local rain water in the Turlock area (Figure 6). The stable isotopes clearly indicate that the groundwater produced at these drinking water wells derives from Sierra Nevada runoff, which is transported to the Central Valley by perennial rivers including the Tuolumne River. Under pre-modern conditions, annual flooding and losing reaches of the river(s) likely recharged the northeastern Central Valley groundwater basins. Under present conditions, recharge is dominated by irrigation return flow, with a supply of Tuolumne River water from the Turlock Irrigation District. Stable isotopes values in Tuolumne River water from a sample in Modesto were -11.78‰ and -84.8‰ in June of 2013 (Harms, 2015), in close agreement with the values measured in wells.

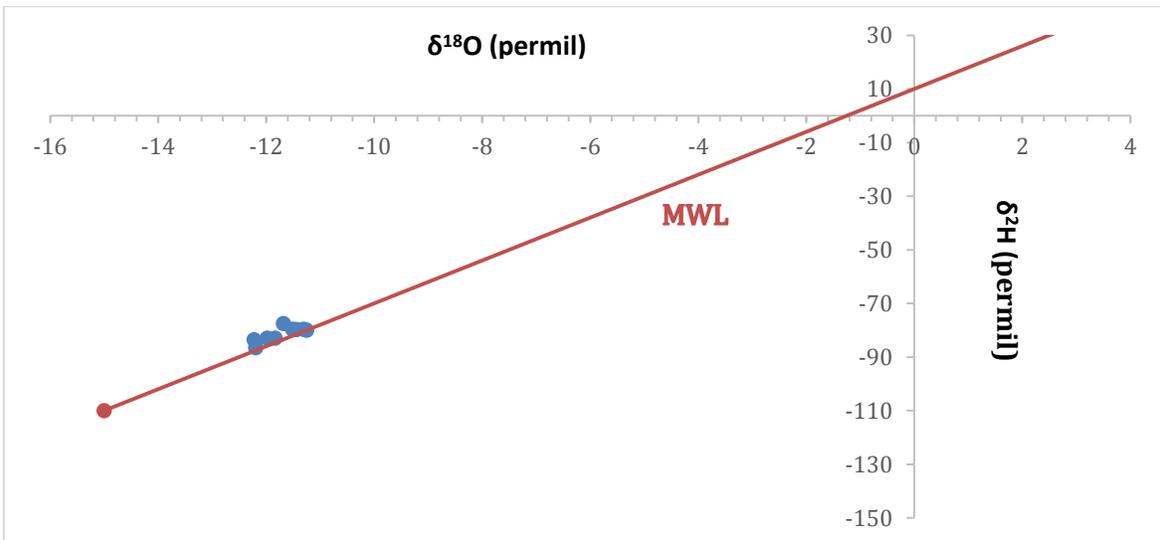


Figure 6. Results for stable isotopes of the water molecule, showing a tight grouping for all wells and little deviation from the Global Meteoric Water Line.

Major anions and cations are plotted on a Piper diagram in Figure 7. Charge balance between major anions and major cations was within 7% for all samples. Groundwaters are of the Ca-Mg-HCO₃⁻ type, with a discernible mixing trend between a high HCO₃⁻/low Cl⁻ endmember and a lower HCO₃⁻/higher Cl⁻ groundwater. Well 36 is characterized by much higher concentrations and proportions of Cl⁻ and Na⁺ and much lower concentrations and proportions of SO₄²⁻ and NO₃⁻ than all other wells.

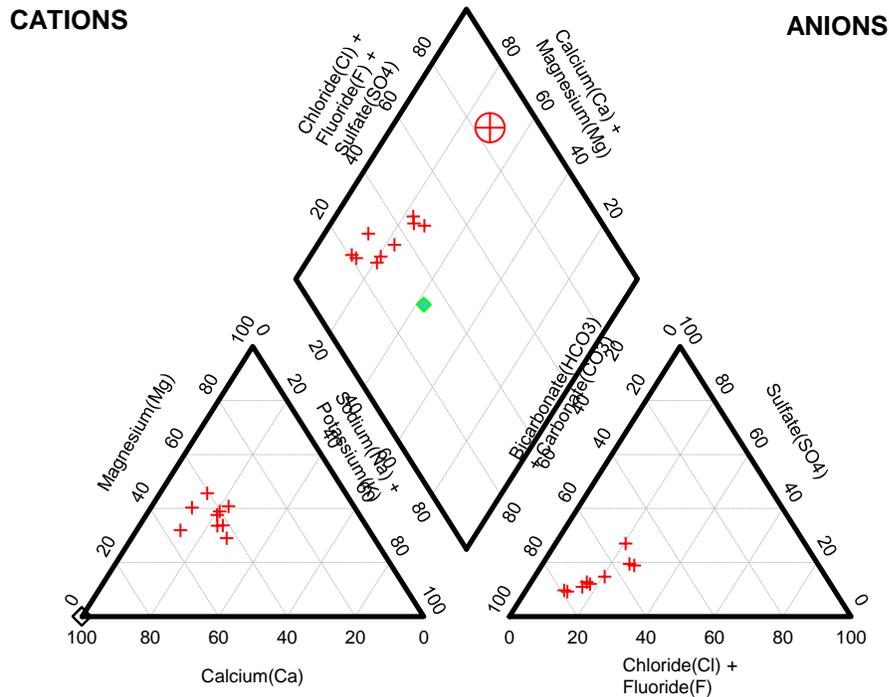


Figure 7. Major anion and cation percentages for all wells plotted on a Piper diagram.

3.2 Nitrate, Excess Nitrogen, and Isotopes of Nitrate

Nitrate concentrations range from 15 to 38 mg/L as NO₃⁻ (except in Well 36 which has a concentration of 1.1 mg/L) and the concentrations measured at LLNL agree closely with recent values from the CDPH database on GeoTracker (Figures 8 and 9). GeoTracker data reveal increasing trends for nitrate in wells 4, 8, 14, 32, 35, and, recently, in Well 29 (figure 9), which are a cause for concern with respect to the drinking water supply. There are several lines of evidence for a low natural, or background nitrate concentration for the Turlock area. Visser et al. (2012) examined nitrate concentrations in wells that produce groundwater that recharged more than about 60 years ago (identified by tritium concentrations below the detection limit) that also produce non-anoxic groundwater (to filter out groundwater that may have experienced denitrification), and found that the median nitrate concentration was only 3 mg/L for Central Valley wells. Furthermore, the low concentration measured in Well 36, and low starting concentrations for several of the wells, indicate that pre-modern nitrate concentrations were likely only 1-2 mg/L. Increases in nitrate observed in wells over the last few decades can therefore be attributed to anthropogenic sources.

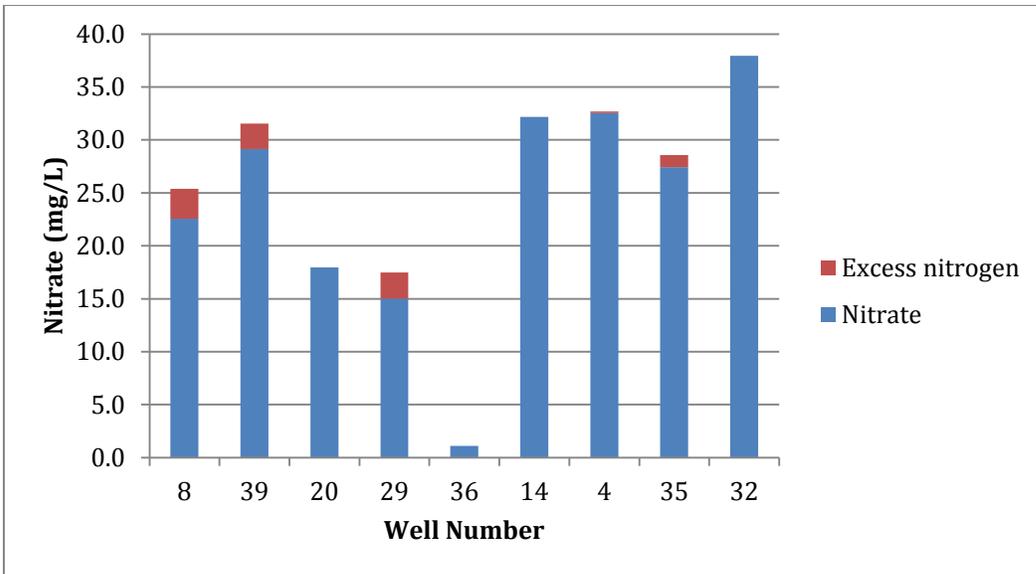


Figure 8. Graph shows both measured nitrate concentrations and calculated excess nitrogen as equivalent nitrate.

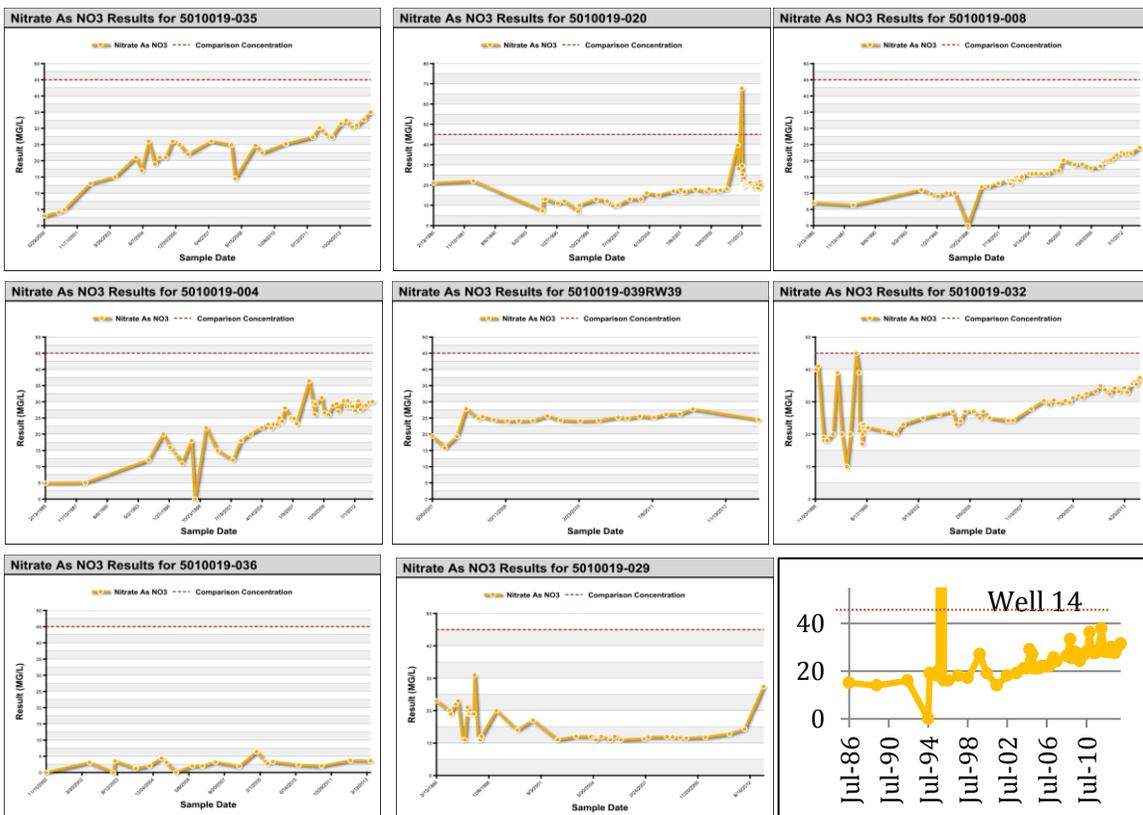


Figure 9. Nitrate concentration histories for the nine wells included in the study (data from: geotracker.waterboards.ca.gov/gama)

The likely source(s) of nitrate are identified by examination of the stable isotopes of nitrate. Figure 10 is the often-used diagram showing the typical fields for different possible sources of nitrate in $\delta^{15}\text{N-NO}_3/\delta^{18}\text{O-NO}_3$ space. The fields for N sources that undergo nitrification ('manure and septic', 'soil N', and 'NH₄ in fertilizer') have been adjusted according to the likely local range for $\delta^{18}\text{O-NO}_3$, (based on observed $\delta^{18}\text{O-H}_2\text{O}$ values and the assumption that 2 atoms of O come from H₂O and 1 atom of O comes from atmospheric O₂ during nitrification; ref). Nitrate in wells from Turlock falls in a relatively narrow range, between -4.6‰ and -8.4‰ for $\delta^{15}\text{N-NO}_3$, and between -0.1‰ and +1.9‰ for $\delta^{18}\text{O-NO}_3$ (except Well 36 which has a $\delta^{18}\text{O-NO}_3$ value of +5.2‰). Most of these values fall in a range of overlap that includes ammonium fertilizer, soil N and animal waste sources. The isotope results are consistent with an inorganic fertilizer source, which is likely, considering the land use history in the Turlock area and the requirements for inorganic N fertilizers for the main crops (originally, mainly alfalfa and more recently, almonds).

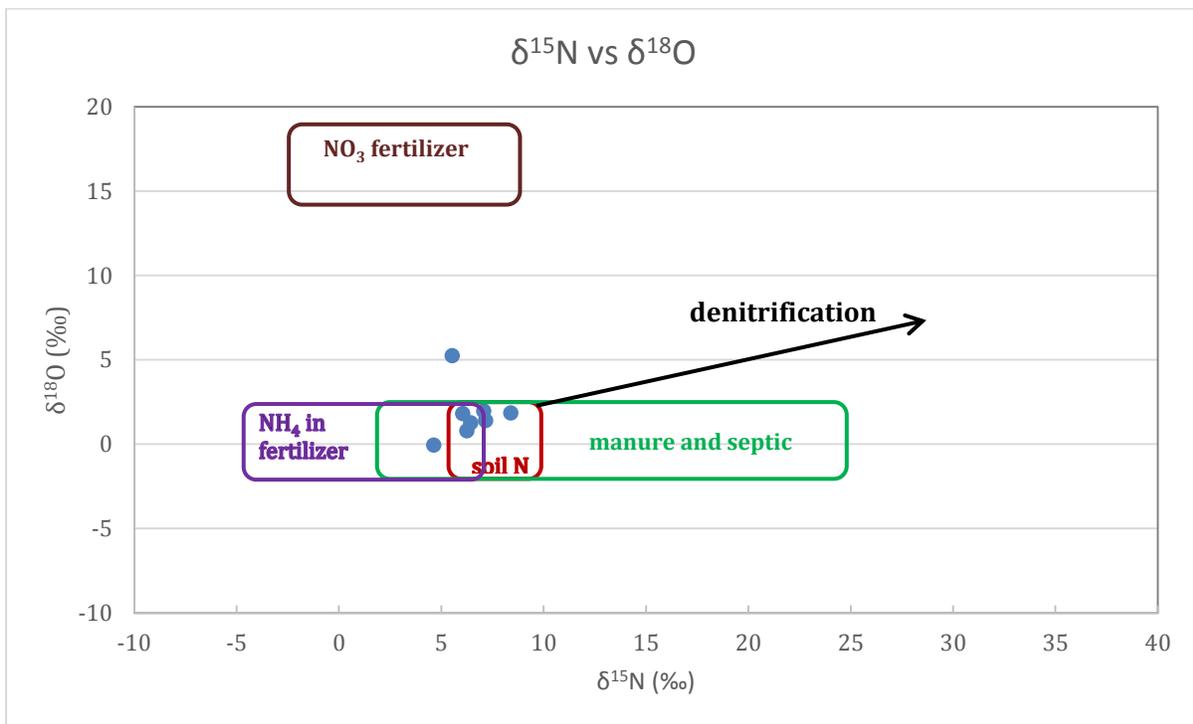


Figure 10.

Interestingly, although the range is not large, the sample results do fall along a trend with a slope of approximately $\frac{1}{2}$ ($R^2 = 0.54$), suggesting that the nitrate isotopes have been altered by denitrification and that the original source signature is at the low end of the range for $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$. However, it is likely that any denitrification takes place in the vadose and not in the saturated zone. The evidence for concluding that saturated zone denitrification is not important comes from measurement of dissolved excess nitrogen, the end product of denitrification. Major dissolved gas species including nitrogen and argon were analyzed by membrane inlet mass spectrometry (MIMS), which allows a distinction to be made between atmospheric nitrogen and nitrogen from saturated zone denitrification. Measured nitrogen to argon ratios are consistent with atmospheric ratios. As shown on figure 8, excess nitrogen concentrations are quite low and could be zero within the propagated uncertainty of the measurements. Denitrification requires the presence of an anaerobic

environment and an electron donor, usually organic Carbon. In the Turlock samples, dissolved oxygen is present at the 2-3 mg/L level in all but Well 36 and total organic Carbon concentrations are low, at ≤ 1 mg/L. Since conditions are not conducive to denitrification, once nitrate reaches the water table, it likely moves conservatively in this aquifer system. Well 36 presents a special case inasmuch as dissolved nitrogen was detected in excess of atmospheric nitrogen, however the most likely source of the additional nitrogen is magmatic, rather than from denitrification (see further discussion of magmatic gas signatures below).

3.3 Age Tracers and Age Distributions

The shortest lived of the applied tracers, ^{35}S , was not found above the detection limit in any of the samples. This result indicates that the 7 wells sampled for this isotope do not produce water that entered the saturated zone within an approximately 18 month period prior to sampling. Considering the deep top perforations of the wells, this is not a surprising result.

The tracer with the next longest half-life, ^{85}Kr , likewise was not found above the detection limit in any of the 5 wells sampled for this isotope. Based on the detection limit of x, this result means that at most 14% of the produced water recharged the aquifer within the last 20(?) years. This result provides an important constraint on the groundwater distribution and the projected response time for changes in nitrate loading to be observed at the wells.

Tritium was analyzed in all nine samples and was found above the detection in all but Well 36 (figure 11). Concentrations above the detection limit fall into two groups, between 2 and 3 pCi/L and between 4 and 6 pCi/L. All of the results are well below the tritium concentration of 10.2 pCi/L observed in the present-day Tuolumne River (Harms, 2015), which is the presumed main source of recharge. Still, detectable tritium in 8 of 9 wells indicates that some portion of the produced water recharged the aquifer system after 1950.

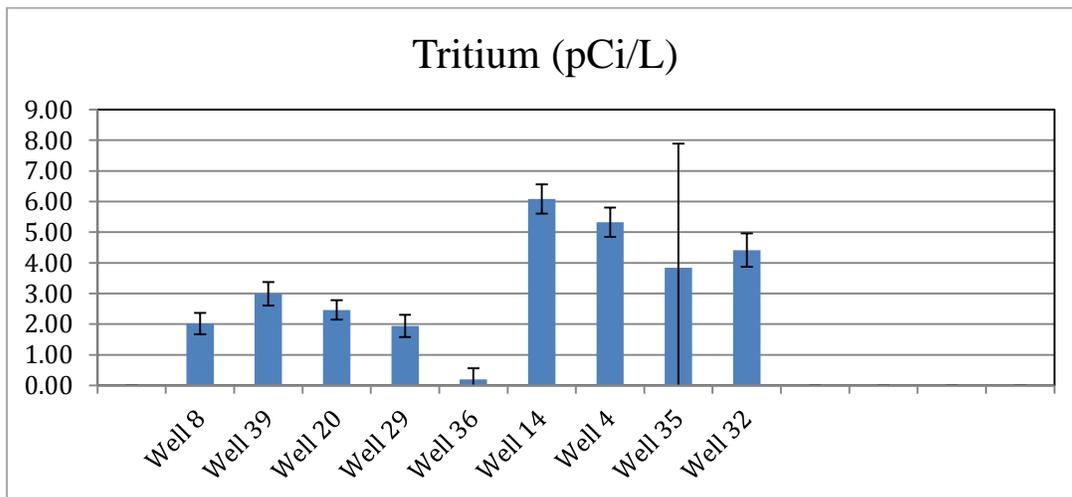


Figure 11. Results of tritium analyses shown with 1 sigma uncertainties.

Tritium-helium groundwater ages, shown on figure 12, are calculated by the method described in Visser et al., 2014. In Turlock samples, low tritium concentrations, high terrigenous helium concentrations, and small mantle helium contributions in several samples lead to large uncertainties in the calculated ages. Figure 12, which shows the relationship between predicted tritium

concentrations for the year of recharge and tritium measured in precipitation, with all but one sample falling well below the precipitation curve, makes clear the large amount of dilution of tritiated groundwater by tritium-dead groundwater. In spite of the significant differences in tritium concentrations and high uncertainties for some samples, mean, apparent tritium-helium groundwater ages, fall in a relatively narrow range between 39 and 57 years for 7 of 8 samples for which ages could be determined. Tritium concentrations are therefore affected by the bomb pulse, in addition to being strongly affected by dilution with tritium-dead groundwater. The modern groundwater component in these samples (present in all except Well 36) therefore has a mean age of almost 50 years, on average, and comprises a minor fraction of the groundwater, as discussed below.

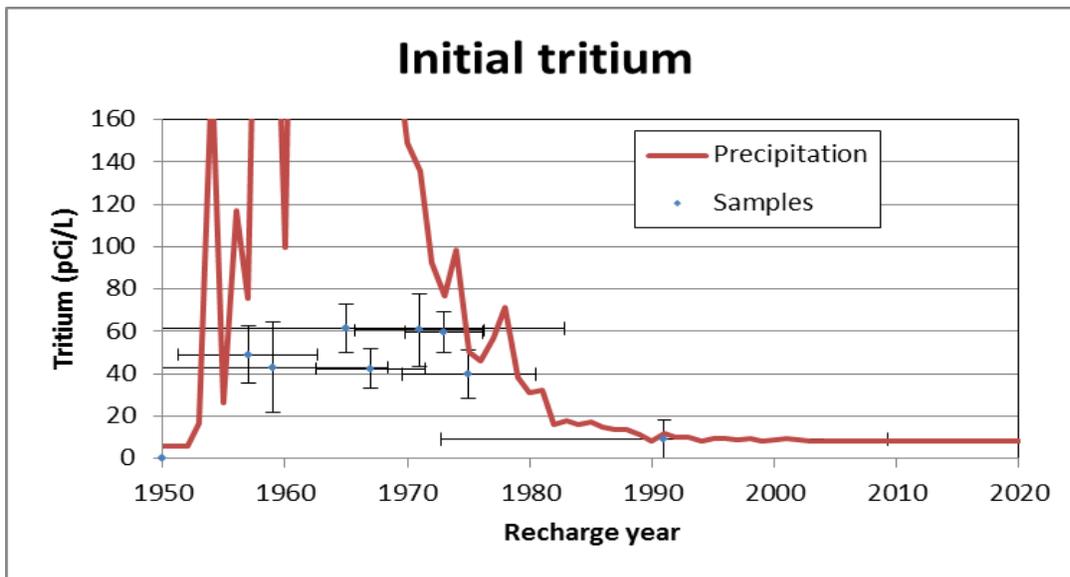


Figure 12.

Determining the mean, apparent age of pre-modern groundwater is fraught with even greater uncertainty than calculating the tritium-helium age of modern groundwater. The applicable tracers, radiogenic ^4He and ^{14}C , are complicated by a poorly known production rate and by subsurface reactions that affect dissolved inorganic carbon, respectively. In addition, magmatic He and CO_2 are detectable in some samples.

Figure 13 is a graphical representation of the expected trends in helium isotopes for the various components in groundwater (atmospheric including excess air, tritiogenic, and terrigenic including magmatic and crustal (or terrigenic)) starting with initial values at 1, 1. Turlock samples fall predominantly along the radiogenic trend, with small excursions above the line that can be attributed to tritiogenic and/or mantle components. The y-intercept of the sample trend corresponds to the local, terrigenic helium ratio, in this case 6.2×10^{-7} . Terrigenic helium concentrations range from 124% to 8831% of equilibrium He. The terrigenic helium concentrations are corrected for tritiogenic contributions to helium, but not for magmatic contributions. If a generic crustal accumulation rate of $1 \times 10^{-11} \text{ ccSTP/g/yr}$ is applied to these concentrations, then radiogenic ^4He ages between 5.6ka and 40.3ka (and 401ka for Well 36) are indicated. This simplified calculation of groundwater age does not take into account the variable rates of ^4He production or release into water, which have been documented in many settings.

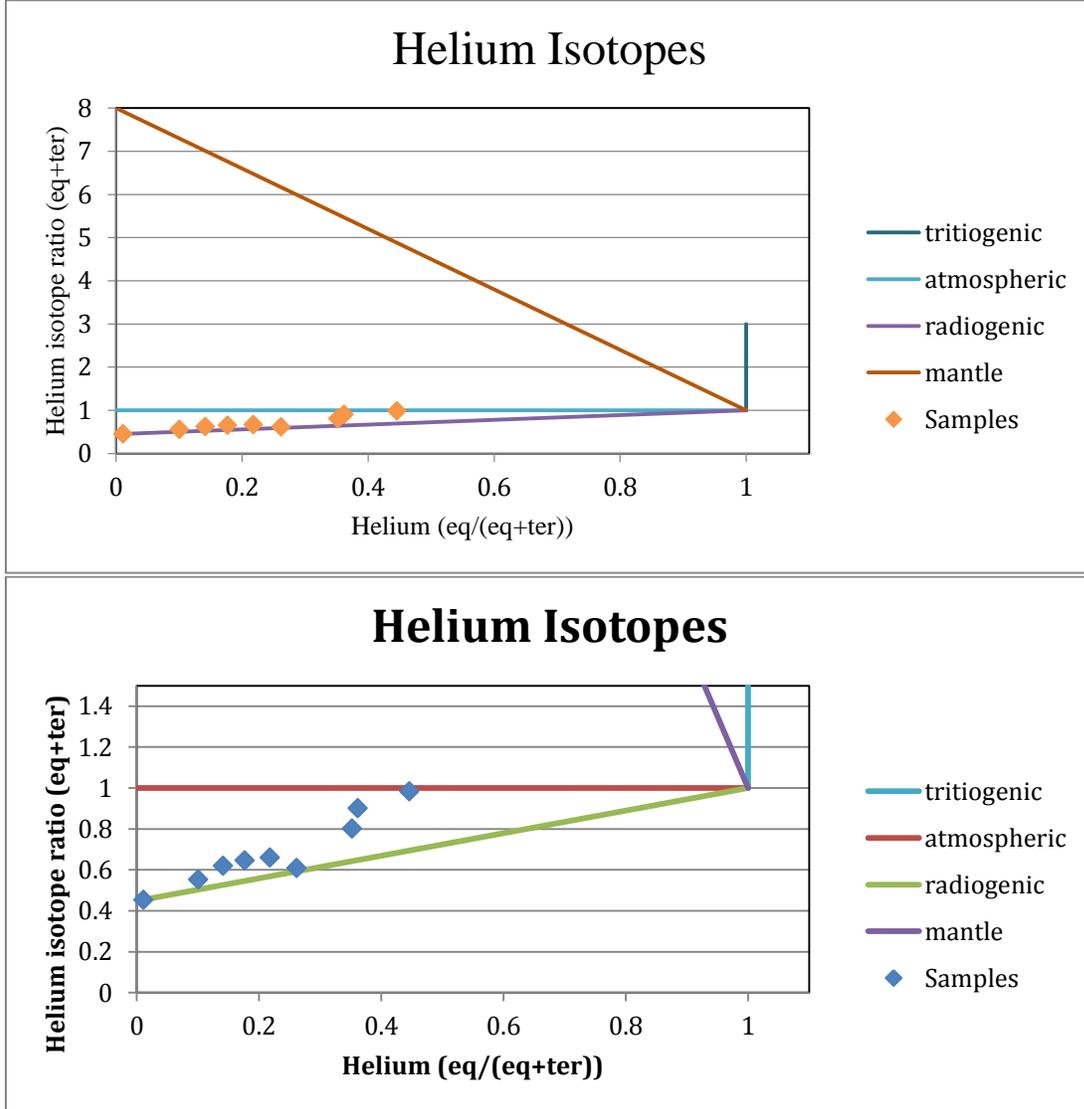


Figure 13.

Complex reactions between atmospheric CO₂ dissolved in groundwater, soil organic matter, and C-containing minerals dictate the DIC concentration and C isotopic composition of groundwater at the water table. Therefore, in addition to the reaction of interest for dating groundwater (decay of ¹⁴C in DIC), subsequent reactions, especially water-rock interaction with carbonate minerals, affect the isotopic composition of DIC. ¹⁴C ages of groundwater are generally considered highly uncertain because these chemical reactions are poorly understood in most settings and are site specific. In particular, determination of the 'initial' activity at recharge is complex. An uncorrected age assumes an initial ¹⁴C activity of 100 pmC, but much lower activities have been observed near recharge areas, especially beneath thick vadose zones or in strongly reducing conditions (Izbicki...).

Schemes developed for adjusting the measured radiocarbon activity for the thermodynamically favorable mass transfer reactions, such as those applied in NETPATH (Plummer et al., (1994), require

information regarding initial DIC and radiocarbon content. However, several studies have shown that although the $\delta^{13}\text{C}$ composition is sensitive to chemical reactions along the flow path, ^{14}C ages are not as sensitive (Davis and Bentley, 1982; Izbicki and Michel, 2004). Except for Well 26, measured $\delta^{13}\text{C}$ values are all close to -14.7‰ (average -14.73‰ , s.d. 0.23‰). The homogeneity of $\delta^{13}\text{C}$ and the fact that -14.7‰ is in line with the predicted value for DIC in an aquifer system in which DIC is derived roughly equally from atmospheric CO_2 +soil organic CO_2 and carbonate dissolution suggests that inorganic carbon is in equilibrium with the aquifer materials at all wells. Furthermore, since this study did not sample any recent recharge, estimating initial chemical and isotopic compositions for is not practical. Therefore, the apparent, uncorrected radiocarbon age shown in Table 3 was calculated assuming an initial ^{14}C activity of 100 pmC and a decay constant of $1.21 \times 10^{-4} \text{ yr}^{-1}$ (half-life 5730 years). Variability in ^{14}C ages likely relates more to mixing of varying proportions of old water rather than variability in the age of the old water component. ^{14}C samples prepared by extracting DIC from aqueous samples on a vacuum line were determined to be contaminated by modern C. However, results from GES and aqueous samples fall along a straight line, allowing samples not collected using the GES to be corrected using the linear relationship.

Table 3. Analytical results for inorganic and organic carbon. Isotope results are for dissolved inorganic carbon.

Well	TIC (mg/L C)	TOC (mg/L C)	$\delta^{13}\text{C}$ (per mil)	$\delta^{13}\text{C}$ StDev	Fraction Modern	\pm	^{14}C age (yr)	\pm
8	24.338	0.905	-14.70	0.4	0.6016	0.0023	4080	35
39	24.577	0.846	-14.58	0.6	0.5895	0.0022	4245	30
20	29.054	0.852	-14.47	2.6	0.5441	0.0026	4890	40
29	27.344	0.748	-14.83	0.0	0.5453	0.0022	4870	35
36	29.423	0.750	-28.62	0.1	0.3962	0.0017	7435	35
14	36.264	1.011	-14.63	0.1	0.8335	0.0029	1465	30
4	29.128	0.870	-15.18	0.4	0.7104	0.0025	2745	30
35	32.373	0.928	-14.48	0.1	0.7227	0.0026	2610	30
32	30.244	0.893	-14.93	0.5	0.6621	0.0024	3315	30

Resulting ^{14}C ages range from 1465 to 7435 years with 4 sample results falling between 4000 and 5000 years. A positive correlation ($R^2=0.61$) exists between ^4He and ^{14}C ages, though the trend is biased by the relationship between the younger grouping of samples and Well 36; when Well 36 is excluded, the correlation is weaker ($R^2=0.21$).

One additional piece of evidence comes from noble gas recharge temperatures, which fall between 16.1C and 18.3C (close to the mean annual air temperature of 17.0C for Turlock), except for Well 36, which has a calculated noble gas recharge temperature of 14.6C . The 3C difference may indicate that recharge that took place under cooler climate conditions, at the end of the last glacial period, about 10,000 years ago. Alternatively, pre-development recharge via spring floods may have been colder than modern recharge, which is now dominated by summer and fall irrigation return flow.

In spite of the uncertainties in the ages of the old components of groundwater in Turlock wells, one can say with certainty that Well 36 does not contain modern groundwater, that modern water is

present in all other wells, that pre-modern groundwater is present in all wells, and that a significant portion of the groundwater recharged before human activity altered the hydrologic system. Both ^4He and ^{14}C point to mean, apparent ages mostly in the 2 to 10 thousand year range. The significance of the presence of pre-modern groundwater is that it contains very low nitrate concentrations, reducing the nitrate concentrations observed in all wells to levels below what would be observed if only modern groundwater were tapped by these wells.

Patterns in age tracer results show relationships to both depth and location for these wells. The example of Well 36, which has a top screen at a depth of 290ft msl and is located in portion of the basin where the Corcoran Clay acts as a confining unit, suggests that the deep, western portion of the basin is isolated from the influence of modern water. In contrast, well 8, on the eastern side, though having a top screen at 350 ft msl, contains some modern water and is experiencing slowly increasing nitrate concentrations. Well 14, on the east side with a top screen at 140 ft msl, has a younger old component (or a smaller fraction of the old component) and is experiencing more rapidly increasing nitrate concentrations.

3.4 Lumped Parameter Models and Nitrate Forecasting

The mean apparent ages discussed so far are reported as single values with uncertainties based on the analytical methods, but they do not account for hydrodynamic dispersion or mixing. These ages are sometimes referred to as piston-flow, advective, or Darcy ages. However, mixing by dispersion can lead to very broad age distributions, even in short-screened wells; mixing in wellbores with long open intervals where multiple aquifers are tapped is likely to broaden age distributions even more. Lumped parameter models may be applied to the interpretation of age tracers, by making simplifying assumptions about possible flow patterns that lead to dispersion and mixing. Jurgens (2011) has made available a spreadsheet program, TracerLPM, which is intended for use in evaluating groundwater age distributions based on age tracers measured in groundwater samples.

TracerLPM contains five LPMs that can be used to determine the age distribution for a sample: piston-flow model (PFM), exponential mixing model (EMM), exponential piston-flow model (EPM), partial exponential model (PEM), and dispersion model (DM). Each of these models can be combined with another model to create a binary mixing model (BMM) for 25 possible BMM combinations (Jurgens, 2011). Models are chosen based on knowledge of aquifer geometry and the hydrogeologic setting. TracerLPM contains decay constants for the tracers applied here, as well as atmospheric input histories for ^3H , ^{85}Kr , and ^{14}C . Production and release rates for ^4He can be specified by entering U and T_h concentrations, and values for aquifer porosity and sediment density.

For Turlock samples, TracerLPM was used in 'Tracer-Tracer' mode to calculate mean ages from model output and to graph sample results along with tracer model output curves. Best fit mean ages and mixing fractions for BMMs are found by minimizing the error between LPM tracer output concentrations and measured concentrations. Results from one scenario, using ^3H and tritiogenic ^3He as tracers and a BMM comprising PFM and EPM LPMs, are shown in Figure 14.

Finally, the 'Age Distribution & Forecasting' workgroup was used for graphing age distributions and for predicting nitrate concentrations in individual wells. A nitrate input curve, developed for nearby Modesto, CA, (Jurgens, 2011) was used as an estimate of nitrate loading to the water table.

Application of multi-tracer methods to determine age distribution in nitrate-contaminated wells

Sample	Sample Date	Method	LPM name	Total mean age (UZ + GW tt)	Unsaturation zone travel time	For BMMs only					Tracers used in optimization	Total error
						Mean age of 1st component	Model parameter of 1st component	Mix fraction of 1st component	Mean age of 2nd component	Model parameter of 2nd component		
110956	6/30/2014	Tracer-Tracer	BMM-PFM-EPM	248.17	1.00	58.00	na	57.20%	500	0.1	3H,3He(trit)	6.02%
110957	7/1/2014	Tracer-Tracer	BMM-PFM-EPM	314.22	0.50	37.90	na	40.31%	500	0.2	3H,3He(trit)	29.35%
110958	7/1/2014	Tracer-Tracer	BMM-PFM-EPM	236.80	0.50	60.50	na	60.00%	500	0.2	3H,3He(trit)	131.76%
110959	7/1/2014	Tracer-Tracer	BMM-PFM-EPM	449.28	0.50	58.60	na	58.55%	1000	0.5	3H,3He(trit)	26.27%
110961	6/30/2014	Tracer-Tracer	BMM-PFM-EPM	274.34	0.50	39.15	na	49.07%	500	0.2	3H,3He(trit)	0.25%
110962	7/2/2014	Tracer-Tracer	BMM-PFM-EPM	314.64	0.50	41.55	na	40.54%	500	0.2	3H,3He(trit)	0.02%
110963	7/2/2014	Tracer-Tracer	BMM-PFM-EPM	349.71	0.50	41.40	na	44.90%	600	0.1	3H,3He(trit)	28.16%
110964	7/2/2014	Tracer-Tracer	BMM-PFM-EPM	299.43	0.50	36.50	na	43.38%	500	0.2	3H,3He(trit)	0.16%
110956	6/30/2014	Tracer-Tracer	BMM-PFM-EMM	289.97	0.50	58.60	na	57.36%	600	na	3H,3He(trit)	0.20%
110957	7/1/2014	Tracer-Tracer	BMM-PFM-EMM	370.15	0.50	30.90	na	40.48%	600	na	3H,3He(trit)	37.17%
110958	7/1/2014	Tracer-Tracer	BMM-PFM-EMM	248.60	0.50	13.50	na	60.00%	600	na	3H,3He(trit)	188.41%
110959	7/1/2014	Tracer-Tracer	BMM-PFM-EMM	374.34	0.50	58.50	na	41.77%	600	na	3H,3He(trit)	2.64%
110961	6/30/2014	Tracer-Tracer	BMM-PFM-EMM	363.96	0.50	59.00	na	43.72%	600	na	3H,3He(trit)	61.94%
110962	7/2/2014	Tracer-Tracer	BMM-PFM-EMM	352.74	0.50	41.00	na	44.32%	600	na	3H,3He(trit)	1.39%
110963	7/2/2014	Tracer-Tracer	BMM-PFM-EMM	352.90	0.50	37.00	na	43.98%	600	na	3H,3He(trit)	39.21%
110964	7/2/2014	Tracer-Tracer	BMM-PFM-EMM	298.16	0.50	34.50	na	53.46%	600	na	3H,3He(trit)	4.25%

Figure 14.

Acknowledgements

We thank the City of Turlock for its enthusiastic participation.

References

- Belitz, K., Dubrovsky, N. M., Burow, K., Jurgens, B., and Johnson, T., 2003. Framework for a Ground-Water Quality Monitoring and Assessment Program for California, Water Resources Investigation Report 03-4166. USGS Water Resources Investigation Report 03-4166, Sacramento, CA, USA.
- Marine, I. W., 1979. The use of naturally occurring helium to estimate groundwater velocities for studies of geologic storage of radioactive waste. *Water Resources Research* **15**, 1130-1136.
- Moran, J. E., Esser, B. K., Hillegonds, D., Holtz, M., Roberts, S. K., Singleton, M. J., and Visser, A., 2011. California GAMA Special Study: Nitrate Fate and Transport in the Salinas Valley. Lawrence Livermore National Laboratory, LLNL-TR-484186.
- Schlosser, P., Stute, M., Sonntag, C., and Munnich, K. O., 1989. Tritogenic ^3He in Shallow Groundwater. *Earth and Planetary Science Letters* **94**, 245-256.
- Singleton, M. J., Esser, B. K., Moran, J. E., Hudson, G. B., McNab, W. W., and Harter, T., 2007. Saturated zone denitrification: Potential for natural attenuation of nitrate contamination in shallow groundwater under dairy operations. *Environmental Science and Technology* **41**, 759-765.
- Arkley, R.J., 2009. The Geology, Geomorphology, and Soils of the San Joaquin Valley in the Vicinity of the Merced River, California. California Division of Mines and Geology. Bulletin 182.
- Casciotti, K.L., Sigman, D.M., Hastings, M.G., Böhlke, J.K., and Hilkert, A., 2002, Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method: *Analytical Chemistry*, v. 74, p. 4905-4912.
- California Air Resource Board (2012). *California's Collaborative Research Efforts on N₂O Emissions from Agricultural Soils* [Power Point Slides].
[http://c-agg.org/cm_vault/files/docs/C-AGG_Presentation-2_29_2012_\(MFitzGibbon-ARB\).pdf](http://c-agg.org/cm_vault/files/docs/C-AGG_Presentation-2_29_2012_(MFitzGibbon-ARB).pdf)
- "City of Turlock, General Plan, 2012; Chapter 7"
<http://www.ci.turlock.ca.us/citydepartments/developmentservices/planning/generalplan/>
- Environmental Protection Agency. *Basic Information about Nitrate in Drinking Water*. February 5, 2014.
Part II: <http://water.epa.gov/drink/contaminants/basicinformation/nitrate.cfm>
Part III:
GAMA Project reports are available on the State Water Board GAMA website:
http://www.swrcb.ca.gov/water_issues/programs/qama/report_depot.shtml

Izbicki, J.A., Stamos, C.L., Metzger, L.F., Halford, K.J., Kulp, T.R., Bennett, G.L., 2008. Source, Distribution, and Management of Arsenic in Water from Wells, Eastern San Joaquin Ground-Water Subbasin, California. U.S. Geological Survey Open-File Report OFR-2008-1272.

Kendall C. (1998) Tracing nitrogen sources and cycling in catchments. In *Isotope Tracers in Catchment Hydrology* (ed. C. Kendall and J. J. McDonnell), pp. 519-576. Elsevier.

Online Archive of California. Aerial photograph of Geer Road and Monte Vista intersection in Turlock, California, circa 1969.

<http://oac.cdlib.org/ark:/13030/kt7p30262d/?brand=oac4>

Phillips, S.P, Green, C.T., Burow, K.R., Shelton, J.L., Lewis, D.L., 2007. Simulation of Multiscale Ground-Water Flow in Part of the Northeastern San Joaquin Valley, California: Scientific Investigation Report 2007-5009.

Roberts, S.K., 2014. *Extraction and Analysis of ¹⁴C in Groundwater Samples*. Lawrence Livermore National Laboratory Standard Operating Procedure.

Sbranti, J. N. "Falling Groundwater Levels Pose Problems for Region." *The Modesto Bee* [Modesto] 13 Oct. 2013: n. pag. Print.

Singleton, M.J., Woods, K.N., Conrad, M.E., DePaolo, D.J., and Dresel, P.E., 2005, Tracking sources of unsaturated zone and groundwater nitrate contamination using nitrogen and oxygen stable isotopes at the Hanford Site, Washington: *Environmental Science and Technology*, v. 39, no. 10, p. 3563-3570.

Singleton, M.J., Moran, J.E., 2009, Using dissolved noble gas and isotopic tracers to evaluate the vulnerability of groundwater resources in a small, high elevation catchment to predicted climate changes: Livermore, Lawrence Livermore National Laboratory LLNL-JRNL-418084, 10 p.

Stanislaus County Agriculture Crop Report. 2012

State Water Resources Control Board Division of Water Quality, GAMA Program. Groundwater Information Sheet, Nitrate. August 2010.

http://www.waterboards.ca.gov/water_issues/programs/gama/docs/coc_nitrate.pdf

Turlock Groundwater Basin Association (TGBA), 2008, Turlock Groundwater Basin, Groundwater Management Plan, prepared for Turlock Irrigation District, March.

Uriostegui, S., Bibby, R., 2013. Recovery of ³⁵S-SO₄ in MAR Groundwater and Surface Water Samples for Radiometric Analysis. Unpublished.

Visser, A., Moran, J.E., Singleton, M.J. and Esser, B.K. (2014) "Geostatistical analysis of groundwater age and other noble gas derived parameters in California groundwater" LLNL-TR-DRAFT-558107, report to the State Water Resources Control Board 56 pp.

Visser, A. Moran, J.E., Aql, R., Singleton, M.J., Esser, B.K. (2013) Examination of Water Quality in "Tritium-Dead" Drinking Water Wells. LLNL-TR-558107, 54pp.